# THE CHEMICAL EXAMINATION OF WATER, FUEL, FLUE GASES AND LUBRICANTS: A COURSE FOR ENGINEERING STUDENTS. CHEMISTRY 16, AS GIVEN IN THE DIVISION OF APPLIED CHEMISTRY AT THE UNIVERSITY OF ILLINOIS

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The Chemical Examination of Water, Fuel, Flue Gases and Lubricants: A Course for Engineering Students. Chemistry 16, as Given in the Division of Applied Chemistry at the University of Illinois by S. W. Parr



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Trieste

# THE CHEMICAL EXAMINATION OF WATER, FUEL, FLUE GASES AND LUBRICANTS

A COURSE FOR ENGINEERING STUDENTS

CHEMISTRY 16

As given in the Division of Applied Chemistry at the

UNIVERSITY OF ILLINOIS

BY

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1916

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## PART I:—LECTURES



## PART II:—LABORATORY METHODS.

## PRELIMINARY STATEMENT

This work is intended primarily for Juniors in Mechanical and Railway Mechanical Engineering at the University of Illinois. From the chemical standpoint, it is a very serious problem to know what may profitably be attempted in the way of analytical methods in the case of students whose chemical experience is meager. But, however unsatisfactory the amount of preliminary training, it is obvious that the curriculum in Engineering courses is already overcrowded, hence the obtaining of a better prerequisite in chemistry is well nigh impossible. The work as herein outlined is the result of ten years of effort to make the most of the situation. It would be quite too much to claim that in the evolution of the work a satisfactory status has been attained. It is hoped, however, that the course will at least help the engineer to a better understanding of the literature of the topics considered and also to an appreciation and, consequently, a more intelligent use of data which may come into his hands from the chemist. It may not be out of place to state further that the course, which, at the first, was inaugurated with no little misgiving, has more than justified the experiment. For this result credit is due the students, who, from year to year have carried the work through with a responsiveness which has been the main stimulus in developing this outline into its present form.

Part I is a synopsis only of the lectures given. Part II consists essentially of laboratory directions for the analytical methods there undertaken. The time allowance for lectures, quizzes, and laboratory is nine hours per week for 18 weeks. The amount of work as outlined is such that the average student covers the ground in the time prescribed.

Special acknowledgement is due Dr. H. J. Broderson for suggested improvements in the present edition and for valued assistance in the reading of proof.

# PART I

## DESCRIPTIVE OUTLINE

## CHAPTER I

### Boiler Waters

#### Their Examination, Character and Treatment.

*Water Analysis:*—Waters are examined for two very different purposes. First, the object may be to determine the potability or sanitary character of the water; and, second, it may be desired to learn the behavior or value of the water for industrial uses. The requirements under each division are very different. In order to be sanitary, a water must be free from certain forms of organic matter which might indicate possible contamination with sewage or furnish a suitable breeding medium for disease germs. Within reasonable limits, the amount of mineral constituent is of little importance. On the contrary, however, the value of a water for industrial purposes depends very largely on the kind and amount of the dissolved mineral substance, while, as a rule, little importance is attached to the organic material present. This is especially true in the case of those waters which are to be used for boiler purposes, and it is this phase of the subject which is of immediate interest.

*Source of the Mineral Constituents:*—Natural waters in passing through the soil come in contact with certain products of decomposition and decay. Some of these substances, notably carbon dioxide, humic acid, etc., are taken up by the waters, in which condition their power to dissolve mineral matter is greatly increased. In this way the decomposition of feldspar, limestone, etc., is constantly going on, the result to the percolated water being that there is taken into solution varying quantities of silica, salts of iron, aluminum, magnesium, sodium, potassium, etc. As a rule, therefore, the less contact natural waters have had with the soil, or the more insoluble the earthy matter with which they have come in contact, the smaller will be the amount of mineral constituents dissolved: and, conversely, the deeper the source of supply, the greater the opportunity for dissolving such material, and consequently the greater will be the amount of such substances in solution. For this reason it has been sometimes customary to divide waters into three classes:—

First; *Surface water,*

Second; *Shallow wells and spring waters,*

Third; *Deep wells and artesian waters.*

*Surface waters* are such as are found in lakes, streams, and artificial ponds, and with these might also be considered cistern or rain waters; shallow well waters may be considered as those obtained from wells or borings which extend into the drift not to exceed 30 or 40 feet; while deep well waters may be considered those that are obtained from a depth of over 100 feet. These divisions are not sharply drawn, and, indeed, the classes merge into each other. This is more readily seen from the fact that many streams, for a large part of the year at least, are fed by waters which have their source in tile drains and springs. The system of underground drainage so largely carried on in these days, therefore, gives to the waters of smaller streams at least many of the characteristics of the water from the shallow wells. This feature is more pronounced during the dry months of the year, as, for example, in the late summer and fall. The amount of mineral matter, therefore, varies inversely as the volume of water in these minor streams. On the other hand, large bodies of water and larger streams, especially those in districts where they come in contact with the more insoluble formations, are remarkably free from mineral matter. This is especially characteristic in the waters of Lake Superior, and in many of the rivers of the north-central region of the United States. In certain regions, also, as in the delta of the Mississippi, water-bearing sands are sometimes found at very considerable depths, but with extremely small amounts of mineral matter present.

It will be seen from the above discussion that any classification based merely upon the source of a water will have little practical value. Before attempting any classification, however, based upon the character of the dissolved mineral constituents it will be necessary to review the processes by which these substances become a part of the water, and to note their properties and behavior under the conditions of actual use in steam boilers.

*Chemical Characteristics of the Mineral Constituents*:—Calcium carbonate, $CaCO_3$, and magnesium carbonate, $MgCO_3$, are the chief constituents of lime rock. Finely divided particles of these substances exist throughout all the clayey deposits of the drift region. The percolating water holding carbon dioxide, $CO_2$, in solution has the property of a weak acid, $H_2O + CO_2 = H_2CO_3$, and in this form is a solvent for the above substances, forming *bicarbonates,* thus:

$$CaCO_3 + H_2CO_3 = CaH_2(CO_3)_2$$
$$MgCO_3 + H_2CO_3 = MgH_2(CO_3)_2$$

These dissolved bicarbonates are readily broken down by heat, thus:

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2$$

The water alone with the carbon dioxide gas driven out of it is not a solvent for calcium carbonate, and the latter is precipitated.

Feldspars of various sorts are usually distributed throughout the drift deposits. These also are slowly decomposed by carbonated waters thereby adding to the water compounds of sodium, potassium, iron and aluminum, as well as hydrated silica, which is also soluble. The general type of this reaction may be shown, thus:

$$\underset{\text{FELDSPAR}}{Al_2O_3.K_2O.6SiO_2} + 2H_2CO_3 = \underset{\text{KAOLIN}}{Al_2O_3.2SiO_2.2H_2O} + K_2CO_3 + 4\,SiO_2$$

In this way complex or impure rocks may, upon their decomposition, yield small quantities not only of lime and magnesium in solution as bicarbonates, but also iron in a bicarbonate form, as well as salts of sodium, potassium, and silicic acid. This result would be more readily understood if we were to enter into a study of the composition of the drift, especially of a region like this where the glacial clay has a very considerable admixture of ground rock such as feldspar, hornblend, mica, dolomite, etc. Moreover, since all drift formation has been deposited in contact with or by means of sea water, we expect a greater or less amount of mineral substances to be present due to such water; namely, sodium chloride, calcium sulphate, etc.

*Solubility of Gypsum:*—We are familiar with the solubility of sodium chloride, but calcium sulphate or gypsum is also soluble, although to a less degree, and this without the aid of carbon dioxide. Its solubility, for example, may be illustrated by the following table:

TABLE I

SOLUBILITY OF GYPSUM

$(CaSO_4 + 2H_2O)$.

1 part dissolves in about 500 parts of water at ordinary temperature
1 part dissolves in about 1200 parts of water at 250 Degrees F.
1 part dissolves in about 1800 parts of water at 300 Degrees F.
1 part dissolves in about 3800 parts of water at 325 Degrees F.

From the above facts it may be readily understood how the mineral constituents come to be dissolved in all underground waters. The kind, amount, and properties of these substances indicate directly the behavior of a water when used for boiler purposes. Almost without exception their presence is objectionable for reasons which will be evident from the following discussion.

*Effects of Impurities:*—The difficulties which attend the use of water in the generation of steam are three in number:

First, *mineral scale* is formed upon the shell, flues, and sheets; second, *foaming* or *priming* may occur; and, third, the water may have *corrosive action* and weaken the metal of which the boiler is composed.

The constituents of a water, therefore, naturally group themselves under these three heads:

1. Scaling Ingredients.
2. Foaming Ingredients.
3. Corrosive Ingredients.

*Scaling Ingredients:* Scaling ingredients are always considered as including silica and any combination of iron, aluminum, calcium, and magnesium. Since the formation of scale is the most common and perhaps the most evident difficulty which accompanies the use of a boiler, it has sometimes been made the basis of a classification for waters. At a meeting of the American Association of Railway Chemists at Buffalo, New York, May 24, 1887, the following schedule of classification was adopted. Waters containing varying quantities of scaling material per United States gallon were graded as in the table below:

TABLE II

CLASSIFICATION OF WATERS BY THE ASSOCIATION OF RAILWAY CHEMISTS

| | |
|---|---|
| Below 8 grains | very good |
| 8 to 15 grains | good |
| 15 to 20 grains | fair |
| 20 to 30 grains | poor |
| 30 to 40 grains | bad |
| over 40 grains | very bad |

In this table the first line was added by the C. B. & Q. Ry. to fit the case of Lake Michigan water, which has approximately 8 grains or less per gallon.